The synthesis of $Mn(bR_3Pc)_nX_2$ (bR_3Pc = tetramethyl-2-butenediylidenebis(triorganophosphorane)-1,2,3,4-tetracarboxylate; $n = 1$ or 2) complexes from the reaction of $Mn(phosphine)_nX_2$ ($X = I$, NCS) with dma (dma = dimethylacetylenedicarboxylate) or the reaction of MnX_2 with bR_3Pc

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Abstract

Adducts of the type $Mn(bR_3Pc)_nX_2$ ($n = 1$ or 2; $X = I$ or NCS) can be prepared either from the reaction of the appropriate $Mn(phosphine)_nX_2$ (phosphine = $(4\text{-}CH_3C_6H_4)_3P$, $(4\text{-}CH_3OC_6H_4)_3P$, Ph_2MeP, Ph_3P; $n = 1$ or 2) complex with dma or from the appropriate MnX_2 salt with the preformed bR_3Pc. Elemental analyses, IR, ESR and ^{13}C and ^{31}P NMR spectra have been used to characterise the products and intermediates, and based on these data a structure is proposed for the $Mn(bR_3Pc)_nX_2$ complexes involving coordination of carbonyl groups of bR_3Pc to the manganese atoms. Under the conditions employed in this study it appears that the MnX_2 salts do not directly react with dma.

Introduction

There have been numerous studies of the interactions of transition metal complexes with unsaturated organic ligands; the metal involved is usually 'soft' and frequently in a low oxidation state. The binding of the unsaturated molecule is often variable. For example, alkynes can coordinate via a π-bond, the alkyne bond being approximately perpendicular to the coordination plane [1]; bidentate coordination is also known forming a triangular moiety with the metal [2]; and insertion of, for example, an alkyne such as dimethylacetylenedicarboxylate into a M–L bond (L = H [3], CH_3 [4], halogen [5]).

We have investigated the binding of manganese(II) phosphine complexes, $Mn(phosphine)X_2$, to small molecules such as molecular oxygen [6], carbon monoxide [7], nitric oxide [8], sulfur dioxide [9] and carbon dioxide [10]. We have also shown that the $Mn(phosphine)X_2$ complexes can form 1:1 adducts with unsaturated molecules such as ethylene [11] and tetracyanoethylene [12]. We report here an extension of these studies to the substituted alkyne dimethylacetylenedicarboxylate, $CH_3O_2CC\equiv CCO_2CH_3$ (dma).

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Results and discussion

Reaction of $Mn(phosphine)_nX_2$ ($n = 1$ or 2) with dma

The 1:1 reaction of the pale pink (X = I) or white (X = NCS) manganese(II) monophosphine complexes with dma in n-pentane under argon yielded the yellow–orange products, whose elemental analyses correspond to a 1:1 adduct $Mn(phosphine \cdot dma)X_2$, Table 1 (see 'Experimental'). The resulting dma adducts are quite stable to dry air, but gradually decompose in the presence of moisture; they are very sparingly soluble in organic solvents. Subsequent investigations (see below) show that the reaction of the phosphine complex with dma results in a reaction at the phosphine, and not the metal, to form a new ligand: tetramethyl-2-butenediylidenebis(triorganophosphorane)-1,2,3,4-tetracarboxylate, bR_3Pc.

The IR spectra do not exhibit bands assignable to the alkyne group, but $\nu(C=C)$ absorptions appear in the 1600–1530 cm^{-1} region, Table 2. Bands assignable to $\nu(C=O)$ appear at *c.* 1740 and 1690–1640 cm^{-1}, and to $\nu(C-O)$ at *c.* 1260 cm^{-1}. The appearance of two $\nu(C=O)$ bands suggests the presence of both uncoordinated and coordinated carbonyls. The electronic spectra in 1,2-dichloroethane exhibit a single intense absorption in the 400–350 nm range ($\epsilon = 3500$–1800 l mol^{-1} cm^{-1}).

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TABLE 1. Physical properties and elemental analyses for manganese(II)-tertiary phosphine-dma adducts

Reactants	Product	R₃P	Compound	Colour	Melting point (°C)	μ_eff/μ_B	C	H	P	Xa	Mn
Mn{(4-CH₃OC₆H₄)₃P}I₂ + dma	Mn(bR₃Pc)I₂	(4-CH₃OC₆H₄)₃P	1	yellow-orange	d128–130[b]	5.86	40.4(40.4)	3.4(3.5)	3.9(3.9)	31.6(31.6)	6.2(6.8)
Mn{(4-CH₃C₆H₄)₃P}I₂ + dma	Mn(bR₃Pc)I₂	(4-CH₃C₆H₄)₃P	2	yellow-orange	d124–126	5.91	42.6(42.9)	3.6(3.6)	4.0(4.1)	33.5(33.6)	7.1(7.3)
Mn(Ph₂MeP)I₂ + dma	Mn(bR₃Pc)I₂	Ph₂MeP	3	yellow	d140–142	5.89	35.8(35.0)	2.7(2.9)	4.1(4.8)	38.7(38.9)	8.1(8.4)
Mn(Ph₃P)I₂ + dma	Mn(bR₃Pc)I₂	Ph₃P	4	yellow	d138–140	5.91	40.3(40.4)	3.3(3.0)	3.6(4.3)	35.7(35.6)	6.5(7.7)
Mn(Ph₃P)₂I₂ + 2dma	Mn(bR₃Pc)₂I₂	Ph₃P	5	yellow	d152	5.93	54.7(53.5)	4.4(4.5)	6.4(5.2)	20.5(21.4)	4.0(4.6)
Mn(Ph₂MeP)(NCS)₂ + dma	Mn(bR₃Pc)(NCS)₂	Ph₂MeP	7	orange	d104–106	5.83	52.0(52.3)	4.0(4.1)	3.9(4.7)	4.4(4.2)	8.3(7.7)
Mn(Ph₂MeP)₂(NCS)₂ + 2dma	Mn(bR₃Pc)₂(NCS)₂	Ph₂MeP	8	yellow-orange	d120–122	5.79	55.5(56.1)	4.2(4.4)	6.7(6.2)	3.6(3.3)	6.9(6.4)

aX = I, N, bd = decomposed. aIsolated as the n-pentane adduct.

The solid state ESR spectra are not very informative, but all exhibit a strong broad band at $g_{eff} = 2.0$, with a medium intensity band at $g_{eff} = 6.0$. This would suggest some association [13], presumably through iodo or thiocyanato bridges. This is confirmed by the appearance of a strong $\nu(CN)$ band at 2143 cm⁻¹ in the IR spectra of the thiocyanate complexes, indicative of Mn–NCS–Mn linkages.

The reaction of the manganese(II) bisphosphine complexes produces only bis(dma) adducts, irrespective of the manganese(II) complexes:dma ratio. This strongly suggests that the number of dma molecule interacting with the manganese(II) phosphine complex depends on the number of phosphine ligands in the latter species and is in keeping with our conclusion that the reaction of dma is with the phosphine and not the manganese. Moreover, we have been unable to promote direct reaction between the MnX₂ (X=I, NCS) anhydrous salts and dma in n-pentane even over a period of two weeks.

Reaction of dma with tertiary phosphines

It is known that alkynes can form adducts with triphenylphosphine [14–16] and triphenylarsine [17], and secondary and tertiary amines [18] also react with alkynes to form highly conjugated adducts. We have therefore synthesised some adducts of dma with some of the phosphines employed in this study, Table 3. The highly coloured adducts exhibit IR absorptions assignable to $\nu(C=O)$ at 1740–1700 cm⁻¹ and $\nu(C=C)$ at 1600–1530 cm⁻¹, Table 4.

The adducts are sparingly soluble in solvents commonly used for NMR experiments. Nonetheless, in acetone ¹³C NMR chemical shifts are exhibited at 15–22 (CH₃ group), 51–53 (ester methoxy group), 129–135 (phenyl group), 139–143 (C=C) and 165–169 (C=O) ppm. The ³¹P NMR spectra exhibited resonances at c. 24–30 ppm, representing significant upfield shifts from the original tertiary phosphine ligands (c. −8 ppm). The electronic spectra of these adducts exhibit a single absorption c. 345 nm ($\epsilon = 8000$ 1 mol⁻¹ cm⁻¹).

Our adducts have spectroscopic properties similar to those of the PPh₃·dma adduct reported by Tebby and co-workers [15], and we assign a similar structure, **A**, to that proposed by the earlier workers.

A

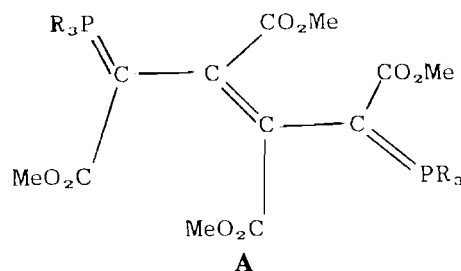TABLE 2. IR data for dma adducts of manganese(II)–tertiary phosphine complexes[a]

| Compound	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	ν(C–O) (cm^{-1})	ν(CN) (cm^{-1})
1	1739(s), 1644(m)	1595(vs), 1565(m)	1260(s)	
2	1739(s), 1694(s)	1594(m), 1533(m)	1254(b)	
3	1739(s), 1694(m)	1594(m), 1572(b)	1265(b)	
4	1739(s), 1689(b)	1594(s,b) 1554(m)	1259(b)	
6	1736(s), 1647(m)	1591(s), 1560(w)	1257(b)	2143(s) 2060(s)
7	1742(s), 1692(m)	1597(s), 1569(b)	1268(b)	2143(s) 2054(m)

[a]vs = very strong, s = strong, m = medium, w = weak, b = broad.

TABLE 3. Physical properties and elemental analyses for the tetramethyl-2-butenediylidenebis(triorganophosphorane)-1,2,3,4-tetra-carboxylates

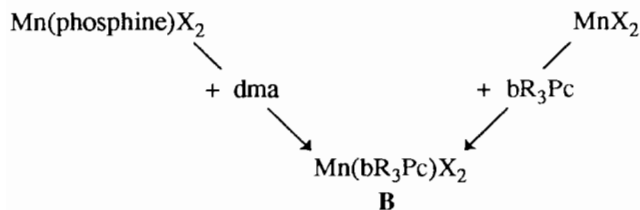| Phosphine used		Colour	Melting point (°C)	Elemental analyses: found (calc.) (%)		
				C	H	P
PPh$_3$	9	yellow	d124	71.0(71.3)	5.3(5.2)	7.8(7.7)
(4-CH$_3$OC$_6$H$_4$)$_3$P	10	orange	d71–73	65.3(65.6)	5.6(5.5)	6.1(6.3)
PPh$_2$Me	11	yellow–orange	d108–110	66.0(66.6)	5.5(5.6)	8.2(9.1)
(4-CH$_3$C$_6$H$_4$)$_3$P	12	yellow–orange	d186	69.3(72.6)	6.0(6.0)	5.9(6.9)

TABLE 4. IR and ^{31}P NMR data for the tetramethyl-2-butenediylidenebis(triorganophosphorane)-1,2,3,4-tetracarboxylates

Compound	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	ν(C–O) (cm^{-1})	^{31}P (ppm)
9	1739(s), 1700(w)	1600(vs), 1533(m)	1254(s,b)	24.9
10	1745(s), 1700(vw)	1583(s), 1533(w)	1259(s,b)	30.3
11	1739(vw), 1698(m)	1600(s), 1566(m)	1259(s,b)	23.9
12	1734(b)	1600(m), 1530(b)	1259(s,b)	24.7
dma	1730(b)		1260(b)	

B
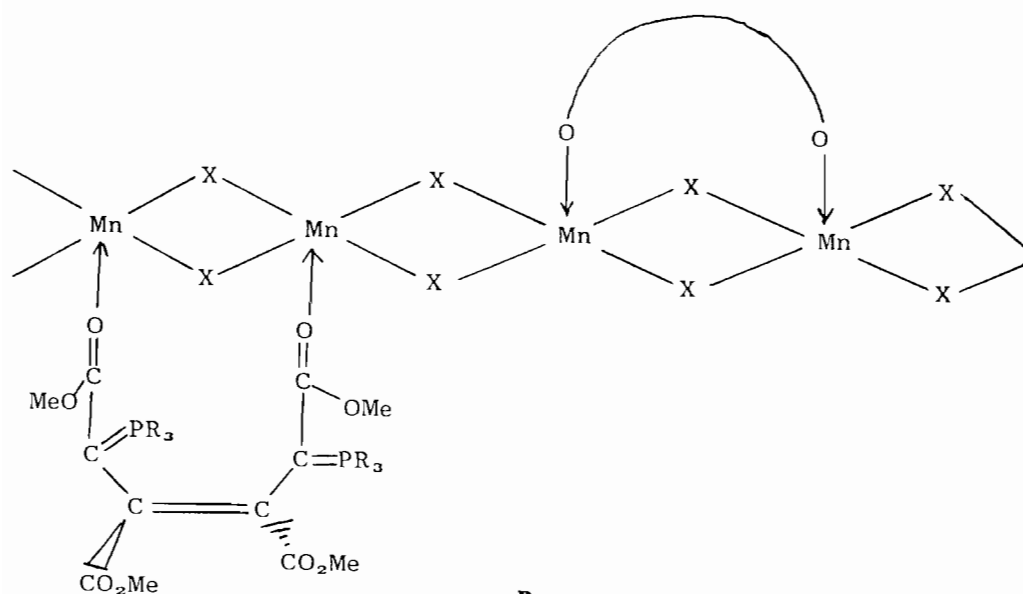
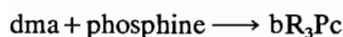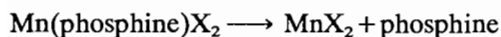*Reaction of $PR_3 \cdot dma$ adducts (bRPc) with anhydrous $MnX_2(X=I, NCS)$*

The reaction of the bRPc ligands with anhydrous manganese(II) iodide or thiocyanate in a 1:1 ratio in n-pentane yielded orange–yellow complexes of stoichiometry $Mn(bRPc)X_2$, **B**, Table 5. The IR spectra of these complexes, Table 6, are strikingly similar to those of the adducts synthesized from the $Mn(phosphine)X_2$ complexes and dma. However, there are some differences in melting points, but this may reflect packing differences arising from the two methods of synthesis:

$$Mn(phosphine)X_2 \qquad\qquad MnX_2$$
$$\searrow \qquad\qquad\qquad \swarrow$$
$$+\ dma \qquad\qquad +\ bR_3Pc$$
$$\searrow \qquad\qquad \swarrow$$
$$Mn(bR_3Pc)X_2$$
$$\textbf{B}$$

In conclusion, it is pertinent to speculate on the structure of the **B** adducts. Taking into account the structure of the phosphine·dma precursor, **A**, it is likely that ligand **A** binds to the polymeric $[MnX_2]$ chain as illustrated. It is also possible that ligand **A** can bind between chains, and this may account for the melting point differences arising from the two methods of synthesis of **B**.

Furthermore, we have previously recognised the lability of the tertiary phosphine ligand in these manganese complexes [6], and we suggest the following mechanism of formation of the complexes reported here:

$$Mn(phosphine)X_2 \longrightarrow MnX_2 + phosphine$$

$$dma + phosphine \longrightarrow bR_3Pc$$

$$bR_3Pc + MnX_2 \longrightarrow Mn(bR_3Pc)X_2$$

Experimental

All manipulations were performed under a dry argon atmosphere. Manganese(II) salts and solvents were dried by published procedures and manganese(II)–tertiary phosphine complexes synthesized by published methods [6, 13]. Dimethylacetylenedicarboxylate was used as purchased (Aldrich Chemicals) without further purification.

(a) Reaction of $Mn(PR_3)X_2$ with dimethylacetylenedicarboxylate, dma: $Mn(PR_3)X_2$ [6] (0.6 mmol, c. 0.4 g) was placed in a pre-dried round bottom flask (250 cm³) equipped with side-arm and tap and the flask

TABLE 5. Physical properties and elemental analyses for adducts of tertiary phosphine–dma with manganese(II) salts

Reactants	Complex	Colour	Melting point (°C)	μ_{eff}/μ_B	Elemental analyses: found (calc.) (%)				
					C	H	P	X^a	Mn
MnI₂+12	13	yellow–orange	d124–126	5.92	40.7(42.9)	3.9(3.6)		33.1(33.6)	7.0(7.3)
MnI₂+11	14	yellow–orange	d128–130	5.90	38.7(40.2)	3.9(3.4)		30.8(31.6)	6.5(6.8)
MnI₂+9	15^b	yellow	d114–116	5.89	43.1(44.3)	3.3(4.2)		31.7(32.2)	6.0(7.0)
MnI₂+10	16	orange–yellow	d110	5.88	34.3(35.0)	3.2(2.9)		34.5(39.0)	
MnBr₂+11	17	orange	d110	5.90	46.1(45.7)	3.7(3.8)		22.8(22.6)	
MnBr₂+10	18	orange	d129–132	5.88	41.2(40.9)	3.7(3.4)		27.4(28.7)	
Mn(NCS)₂+11	19	yellow	d112	5.83	50.8(52.3)	3.6(4.1)	4.1(4.7)	4.4(4.2)	
Mn(NCS)₂+10	20	yellow	d108	5.77	48.4(49.1)	3.9(3.7)	6.0(6.0)	5.8(5.5)	

^{a}X=I, Br, N. ^{b}Isolated as n-pentane adduct.

TABLE 6. IR data for adducts formed between tertiary phosphine–dma and manganese(II) salts

Compound	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	ν(C–O) (cm^{-1})	ν(CN) (cm^{-1})
13	1733(s), 1681(m)	1560, 1540(b)	1259(b)	
14	1739(s), 1665(m)	1589(vs), 1565(w)	1260(s,b)	
15	1739(s), 1689(m)	1583(s), 1550(m)	1259(b)	
16	1739(s), 1667(m)	1583(s), 1533(m)	1260(b)	
17	1734(s), 1664(m)	1560(b)	1260(b)	
18	1739(vs), 1667(m)	1550(s,b)	1248(b)	
19	1739(s), 1658(m)	1586(s,b)	1259	2143(s) 2060(m)
20	1739(m), 1660(m)	1595(s), 1560(m)	1250(b)	2130(s) 2050(s)

flushed several times with argon. n-Pentane(60 cm^3) was added using a pre-dried syringe against an argon stream and the flask flushed three times with argon to remove any dissolved oxygen. An equimolar amount of dma (0.6 mmol) was then added and the flask again flushed several times with argon and the mixture was stirred for 4 days. The yellow–orange solid product was isolated by standard Schlenk techniques, washed with n-pentane and dried *in vacuo*.

(b) The Mn(PR$_3$)$_2$X$_2$ adducts with dma were similarly prepared using a 1:2 molar ratio, respectively.

(c) Tertiary phosphine–dma adducts were synthesised in the same manner as described above. Equimolar amounts of the tertiary phosphine (10 mmol) and dma (0.14 g, 10 mmol) were stirred for *c.* 2 h in freshly distilled n-pentane under an argon atmosphere. The yellow–orange products were isolated and dried as described above to give a final yield of 75–80%.

(d) The reaction of tertiary phosphine–dma adducts with anhydrous manganese(II) salts was performed in the same way as described for Mn(PR$_3$)X$_2$–dma adducts.

Physical measurements

The room temperature magnetic moments were determined using the Faraday method; employing the Oxford Instruments magnetic susceptibility system. ESR spectra were recorded on a Varian Spectrometer, model E9. The spectra were run in the X-band (microwave frequency *c.* 949 GHz) with a modulation frequency of 10^4 Hz. IR spectra were recorded as nujol mulls between Kbr plates (4000–400 cm^{-1} or polystyrene plates 500–200 cm^{-1}) using a Nicolet 5PC FT-IR spectrometer. Solution UV–Vis spectra were recorded using 1 cm path length quartz cell on a Varian/Cary 210 spectrometer.

References

1 G. R. Davies, W. Hewertson, R. H. R. Mais, P. G. Owston and G. G. Patel, *J. Chem. Soc. A*, (1970) 1873.
2 J. O. Glandville, J. M. Stewart and S. O. Grim, *J. Organomet. Chem.*, 7 (1967); M. A. Bennett, G. B. Robertson, P. O. Whimp and T. Yoshidos, *J. Am. Chem. Soc.*, 93 (1971) 3797; U. Rosenthal and G. Oehme, *J. Organomet. Chem.*, 389 (1990) 251.
3 B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, (1969) 2766; T. Blackmore, M. I. Bruce and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1974) 106.
4 A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, (1977) 1384; T. G. Appleton, M. H. Chrisholm, H. C. Clark and K. Yasufuku, *J. Am. Chem. Soc.*, 96 (1974) 6600.
5 T. G. Diulesca, S. Staiar, E. Avram, F. Chiraleu and M. Avram, *J. Organomet. Chem.*, 136 (1977) C15; D. M. Roe, C. Calvo, N. Krishnamachari, K. Moseley and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1973) 436.
6 C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little and K. Minten, *J. Chem. Soc., Dalton Trans.*, (1983) 2147.
7 C. A. McAuliffe, D. S. Barratt, C. G. Benson, A. Hosseiny, M. G. Little and K. Minten, *J. Organomet. Chem.*, 258 (1983) 35.
8 D. S. Barratt and C. A. McAuliffe, *J. Chem. Soc., Chem. Commun.*, (1984) 594.
9 C. A. McAuliffe, D. S. Barratt, C. G. Benson, G. A. Gott and S. P. Tanner, *J. Chem. Soc., Dalton Trans.*, (1985) 2661.
10 D. S. Barratt and C. A. McAuliffe, *Inorg. Chim. Acta*, 97 (1985) 37.
11 G. A. Gott and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, (1987) 2241.
12 G. A. Gott and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, (1987) 1785.
13 R. D. Dowsing, J. F. Gibson, M. Goodgame and P. J. Howard, *J. Chem. Soc. A*, (1970) 1133.

14 L. Horney and J. Hoffman, *Angew. Chem.*, *56* (1956) 473; K. Akiba, T. Yoneyama and N. Inamoto, *Bull. Chem. Soc. Jpn.*, *49* (1976) 2023.

15 M. A. Shaw, J. C. Tebby, R. S. Ward and D. H. Williams, *J. Chem. Soc. C*, (1967) 2442; *J. Chem. Soc. C*, (1968) 1608.

16 J. B. Hendrickson, R. E. Spenger and J. J. Sins, *Tetrahedron*, *19* (1963) 707.

17 A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, (1961) 2126.

18 R. Huisgen, B. Giese and H. Huker, *Tetrahedron Lett.*, *20* (1967) 1883; *20* (1967) 1889.